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SUGGESTED RAPID PROCEDURE FOR HYDROCARBON-TYPE ANALYSIS OF MIDDLE AND HEAVY FRACTIONS OF SYNTHETIC FUELS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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by

J. Beshai* and A.E. George**

ABSTRACT

A literature survey of HPLC methods for hydrocarbon-type separation was carried out to determine their suitability for application to the analysis of synthetic fuel middle and heavy distillates. A procedure applying the methods of Dark and Sautoni wherein the sample is first separated on an NH_2 bonded stationary phase was proposed. The aromatic fraction would be further separated on a μ-Porasil column and the polar fraction on a phenyl bonded stationary phase. Evaluation of various polar bonded stationary phases was also recommended.

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INTRODUCTION

A reliable method for the separation of heavy oil distillates into saturates, mononuclear aromatics, dinuclear aromatics and combined polynuclear aromatics-polar material has been developed by the U.S. Bureau of Mines in conjunction with API project No. 60 (1). This process is time consuming because elution takes place under gravitional force and the weight percent of hydrocarbon types is determined gravimetrically which requires evaporation of solvent.

This method has been modified at the Energy Research Laboratories by scaling down sample size, gel and solvent volumes by a factor of 10 (2). The time of analysis was reduced considerably (typically 2 days per sample) by applying pressure to speed up elution, yet quantitation of the hydrocarbon concentrates was still done gravimetrically which requires evaporation of solvent.

The objective of this report is to investigate the possibilities of accomplishing hydrocarbon-type separations using high performance liquid chromatography to further reduce the analysis time.

LITERATURE SURVEY OF PRESENT METHODS FOR HYDROCARBON-TYPE SEPARATIONS

In 1972 W.A. Dark (3) outlined a procedure for separating petroleum distillates into aliphatic (straight chain, branched paraffins), aromatic, naphthenic (cyclic) and biphenyl compounds on a 4 ft x 2.3 mm I.D. column packed with Porasil T. No mention was made of polar compounds which would be retained on the column and could have been eluted with methylene chloride.

In 1978 Dark (4) separated coal liquids into saturates, aromatics, and polar compounds on a μ-Bondapak NH_2 column. There was some evidence of the separation of aromatics on the basis of the number of condensed rings, but the resolution was poor. The column was backflushed to elute the polar compounds as an unresolved peak. The polar fraction was then further fractionated on a reverse phase μ-Bondapak phenyl column.

Further separation of the aromatic fraction according to the number of condensed rings was also accomplished by Dark (5). Fractions from a preparative chromatographic run on a μ-Porasil column were characterized by LC-MS. A reverse phase μ-Bondapak C_{18} column was used for the separation. The mass spectral data confirmed that the separations performed on μ-Porasil columns were according to ring number.

Suatoni and Swab have applied HPLC techniques both preparatively (6) and analytically (7) to separate crude oils, middle distillates, gasolines, kerosines, fuel oils, residuals, lubricating oils and synthetic crudes derived from coal liquids, shale oils and tar sands into saturates, aromatic and polar fractions. A μ-Porasil column was used for the analytical separation and a Biosil A column for the preparative separation. In the analytical separation, the saturates were eluted after which the column was backflushed to elute the aromatic fraction in a single sharp peak. Without backflushing a broad unresolved peak occurred. For the preparative scale separation, polar compounds were eluted with a 50:50 CH_2Cl_2/acetone mobile phase. No attempt was made to resolve the aromatic peak.

Matsunaga and Yagi (8) have separated aromatic compounds on an alumina column. The model compounds (tetralin, biphenyl, naphthalene, anthracene, acenaphthylene, phenanthrene, anthracene, 1,2-benzopyrene, chrysene) were well resolved, but the oil samples were not.

Chumakov and Lopatenko (9) obtained a separation of saturates, mono- and di-aromatics from middle distillates on a γ-alumina column. There was some overlapping of the saturates and monoaromatic fractions.

C. Reichert and L. Grant (10) separated bitumen into asphaltenes, resins, and a mixture of aromatics and saturates by using a normal phase (Aerograph Micropak C_{10}) and a reverse phase (Aerograph Micropak CN) column in series.

QUANTITATION OF HYDROCARBON-TYPES

Quantitative analysis of aromatic compounds, when ultraviolet detection is used, is difficult as each compound has its own absorptivity. Calibration curves can be drawn using model compounds or by determining calibration factors from standard fractions (6). When an isocractic mode is used, the refractive index response can be related to concentration. A calibration curve is prepared from the response of standards at various concentrations.

A moving wire detector can also be used to detect organic carbon. Drushel (11) found that the results were not as reliable as the results from the refractive index detector.

Although it would be more convenient to determine the weight percentage of the hydrocarbon fractions from the chromatograms, quantitative determination can be made gravimetrically after the retention volumes have been determined.

SUGGESTED SEPARATION SCHEME

For the separation of fossil fuel products into hydrocarbon-types it is suggested that polar bonded sationary phases ($(NH_2)_2$, RCN, ROR) be evaluated. Some commonly used stationary phases are shown in Table 1.

From the literature survey it would appear that either the method developed by W.A. Dark (4,5) for chemical characterization of coal liquids or the method of Suatoni and Swab (6,7) devised for coal liquids, shale oils, crude oils, could be successfully applied. For information on the aromatic ring distribution within the aromatic fraction, a μ-Porasil column could be used. A comparison of retention data obtained on a normal phase column with that from a reverse phase column for oil samples in conjunction with standard compounds will aid in the analysis of peak components.

A schematic describing a suggested hydrocarbon-type separation procedure for a synthetic crude is shown in Fig. 1.

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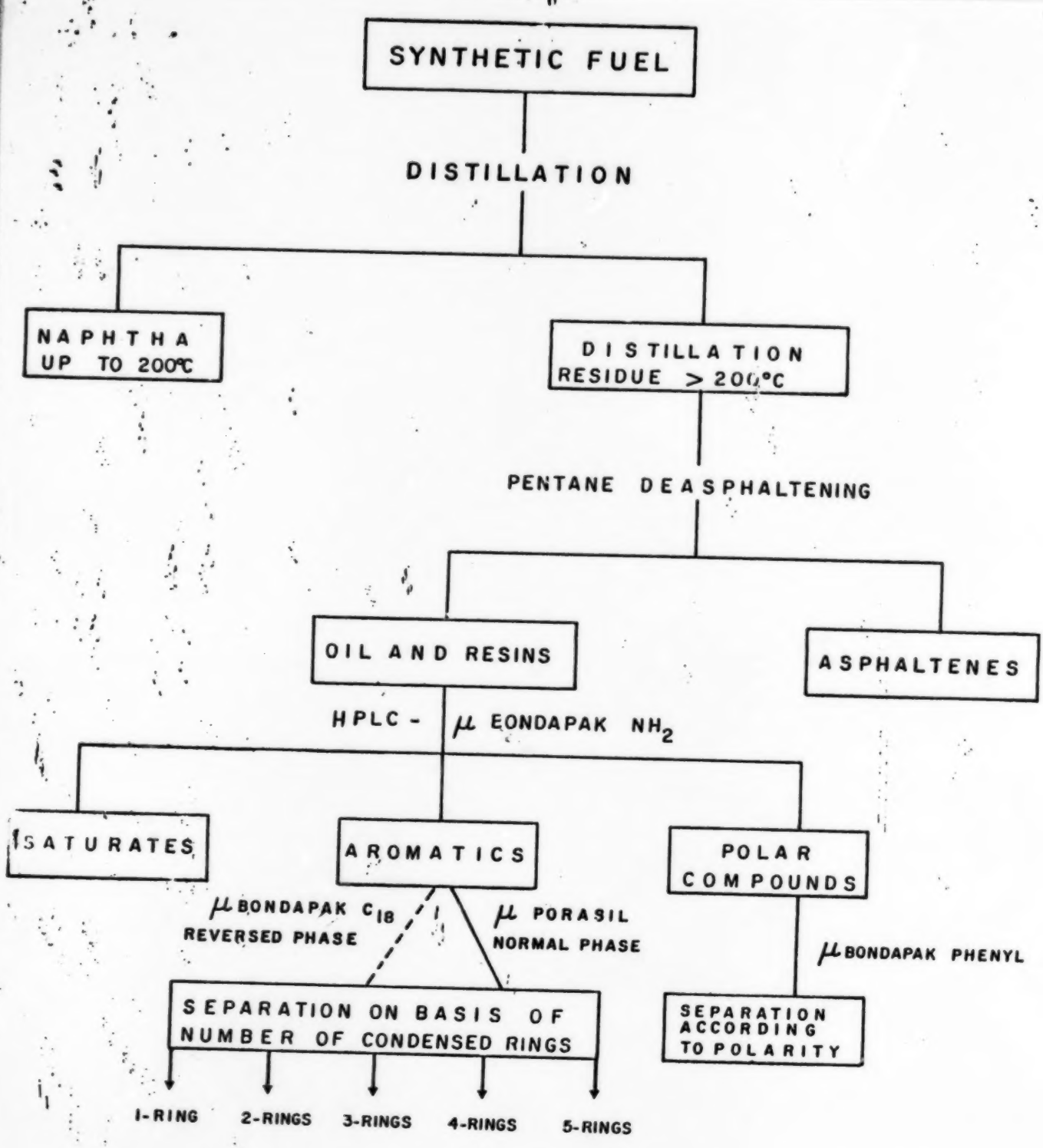
TABLE 1

HPLC Columns Commonly Used for Hydrocarbon-Type Separation

Name	Phase	Functionality	Base Material	Particle Size
μ-Bondapak NH_2	Normal Phase	amino	-Porasil	10 μm
μ-Bondapak Phenyl	Reverse Phase	phenyl	-Porasil	10 μm
μ-Bondapak C_{18}	Reverse Phase	octadecylsilane	-Porasil	10 μm
μ-Porasil	-	-	irregular* silica	10 μm
Biosil A	-	-	irregular* silica	2-10 μm
$(RNH_2)_2$	Normal Phase	diamine	Lichrosorb	10 μm
ROR	Normal Phase	ether	Chromegabond	10 μm
CN	Normal Phase	nitrile	Chromegabond	10 μm

* non-spherical particles



SUGGESTED SCHEMATIC FOR HYDROCARBON-TYPE SEPARATION IN SYNTHETIC FUEL FRACTIONS

FIGURE - 1